

THE INFLUENCE OF SUPPORT ON K PROMOTION OF Ru FOR THE FISCHER-TROPSCH SYNTHESIS

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INTRODUCTION

Ruthenium is known as a good hydrogenation catalyst and has been found to have the highest Fischer-Tropsch (F-T) activity among Group VIII transition metals in producing linear hydrocarbons at high pressure and moderate temperature. Supported Ru, such as Ru/SiO₂ and Ru/Al₂O₃, has been used to produce gaseous and liquid hydrocarbons, (1-3) but such catalysts have been found to give a poor selectivity for olefins and to produce methane as the major product at temperature higher than 260°C. Recent studies have shown that significant improvements in the catalytic selectivity in the F-T synthesis at low pressure can be obtained by metal-support interactions (4) or by alkali promotion (5) of the Ru.

Potassium and potassium salts* have long been used to enhance the activity and the selectivity for both olefinic and long chain hydrocarbons of Fe catalysts. For Ru, such K promotion has been found to activate the chemisorption of di-nitrogen and thus increase the activity of ammonia synthesis at low temperatures and pressures. (6) It has been suggested that this occurs by electron donation to the catalytic metal. Activation of Ru by K promotion has been found to be considerable for both ammonia synthesis and CO hydrogenation reactions if a conductive support, such as graphite, is used. It has been inferred that an electron conductor may facilitate the transfer of electrons from the potassium to the ruthenium. (6 - 8) Earlier research reported that the addition of K to the Ru had no significant effect in changing the catalytic properties of the metal, either supported or non-supported. (9,10) However, Okuhara et al. (5) have recently found that the presence of K in a carbonyl-derived, highly dispersed Ru catalyst enhanced the preferential formation of C₂-C₅ olefins at 260°C but at the same time depressed the activity of the reaction.

This paper reports the results of an investigation into the effect of the support on the influence of K addition on the hydrocarbon selectivity of the Ru metal in the F-T reaction. In this study, different classes of Ru catalysts were prepared using traditional SiO₂ and Al₂O₃ supports, SMSI titania, graphite, and zeolite Y supports.

EXPERIMENTAL

The titania support was from Degussa, and SiO₂ and NaY supports were from Strem Chemicals. The catalysts were prepared by impregnation of the supports with an aqueous solution of RuCl₃ · 3H₂O or by ion-exchange of the NaY zeolite with Ru(NH₃)₆Cl₃. All the impregnated samples were made by the incipient wetness technique. These catalysts were dried in air at 40°C for 50 hours. Ru/Al₂O₃ and Ru/graphite were also obtained from Strem Chemicals. The addition of potassium was made by an impregnation of K₂CO₃ solution to the Ru catalysts followed by drying.

The standard pretreatment used for all the samples consisted of a stepwise heating procedure to 400°C in flowing hydrogen (50 cc/min). The samples were held at 400°C in hydrogen flow for at least 2 hours before cooling to the chosen reaction temperature in the range 250°C to 325°C.

* refer to all different forms of potassium, designated as K in this study.

Kinetic studies were carried out in two similar microreactor systems. The product gas was transferred from the reactor to the sampling valve of the G.C. via a heated transfer line and was analyzed either by a Hewlett-Packard 5750 or by a Perkin-Elmer Sigma 115 Gas Chromatograph equipped with TCD, FID, and Porapak Q columns.

The reactant gases used were H_2 (99.999%), He (99.997%), and a H_2/CO mixture ($H_2/CO = 1$, 99.9%) which were further purified by passing through traps to remove water and metal carbonyl contaminants before passage through the reactors.

The steady state reaction rate was measured after catalyst stabilized. A Hydrogen Bracketing Technique was used in which the reactant stream was replaced by a pure H_2 flow after short reaction periods so as to maintain a clean metal surface. For all the samples studied, the catalytic activities were measured after 30 minutes of reaction and calculated from CO conversions based on CO flow rates coupled with carbon balances on the product stream. The CO conversion was kept below 5% to minimize the effects of heat transfer and concentration gradients. Typical F-T reaction conditions were applied to a variety of supported Ru catalysts at $H_2/CO = 1$, 1 atm pressure, and a space velocity G.H.S.V. of 1800 hr^{-1} .

RESULTS AND DISCUSSION

The catalytic activities and the distributions of hydrocarbons for the various Ru catalysts are presented in Table 1 for a reaction temperature of 280°C . The specific rate of CO conversion for the unpromoted 5 wt% Ru catalysts was found to increase in the sequence: $TiO_2 < Al_2O_3$, $SiO_2 < NaY < \text{graphite}$. The high activity of graphite-supported Ru is consistent with the result found in the literature for graphite-supported Fe in the synthesis reaction. (11) This behavior is probably due to the fact that graphite can enhance electron transfer to the metal. The Ru/ TiO_2 , although having the lowest activity in the series, shows high yields of olefins while methane formation is greatly reduced, as expected. It is obvious that the SMSI behavior is responsible for this superiority in olefin production.

In each case, the addition of K significantly enhanced the fraction of olefinic products (C_2-C_4) for the impregnated Ru catalysts. On the other hand, the rate of the synthesis is decreased by this addition. However, the selectivity of methane formation does not change markedly upon K addition.

The effect of temperature on methane and olefin fractions formed over these Ru catalysts is shown in Figures 1 and 2, respectively. Methane formation normally increases with increasing temperature of the reaction, since the possibility of hydrogenation of the primary surface complex is expected to be greater at higher temperature. A trend towards a decreasing fraction of olefins with an increasing temperature is also to be expected. It is apparent (Figure 2) that methane formation is not affected by the addition of K to the Ru catalysts in the temperature range 250°C to 325°C , except for Ru/ Al_2O_3 . On the other hand, the C_2-C_4 olefin fraction for all the promoted catalysts examined was found to remain essentially independent with increasing temperature. This behavior indicates that the presence of potassium atoms in the vicinity of Ru crystallites may have deactivated some active Ru sites for olefin hydrogenation.

The formation of liquid hydrocarbons (C_5+) over the SiO_2 - and Al_2O_3 -supported Ru catalysts were also greatly enhanced by K promotion (Table 1). The hydrocarbon distribution from the F-T reaction over these catalysts can be fitted into the Anderson-Schulz-Flory equation. The chain growth probabilities calculated both from the slope and from the intercept of the fitted straight line are given in Table 2, designated as P_s and P_i , respectively. Obviously, the addition of K has promoted chain growth on both SiO_2 - and Al_2O_3 -supported Ru. However, it has no effect on higher hydrocarbon formation for the SMSI Ru/ TiO_2 catalyst.

TABLE 1: CATALYTIC PROPERTIES OF Ru CATALYSTS

H ₂ /CO = 1 Temp = 280°C GHSV = 1800 hr ⁻¹ P = 1 atm						
Catalyst	Rate (μmol/sec.gCata.)	HC Selectivity (wt%)			C ₂ = C ₂	C ₃ = C ₃
		CH ₄	C ₂ -C ₄ (ole%)	C ₅ +		
5% Ru/SiO ₂	1.54	64.5	31.0(55) ^a	4.6	0.47	4.0
2.1%K, 5% Ru/SiO ₂	0.15	62.3	32.6(87)	9.0	11.85	4.28
5% Ru/Al ₂ O ₃	1.08	49.1	43.0(61)	7.9	0.66	5.11
2.5%K, 5% Ru/Al ₂ O ₃	0.29	40.2	38.5(98)	21.2	22.40	53.50
5% Ru/TiO ₂	1.34	33.1	49.5(68)	17.4	1.26	7.67
1.1.9%K, 5% Ru/TiO ₂	0.94	29.3	52.3(88)	18.4	4.90	20.80
5% Ru/graphite	3.42	78.2	21.5(4)	0.3	0.05	0.02
2.5%K, Ru/graphite	1.37	65.3	37.7(85)	0	0.73	130.4
5% RuNaY (IW) ^b	3.13	86.7	13.1(5)	0.2	0.1	-
2.5%K, 5% RuNaY	1.20	87.5	11.6(42)	0.9	0.43	-
3% RuNaY (IE) ^c	2.96	89.2	10.8(22)	0	0.20	1.2
1.8%K, 3% RuNaY	2.24	95.7	4.3(18)	0	0.17	1.54

(a) Values in parenthesis are the wt% fraction of olefins in the C₂-C₄ total fraction.

(b) by incipient wetness.

(c) by ion-exchange.

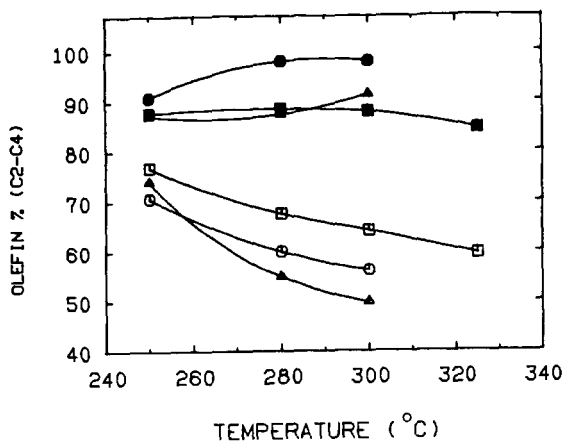


Figure 1 Temperature Dependence of Olefin Production.

Catalyst: Δ Ru/SiO₂ ; \bigcirc Ru/Al₂O₃ ; \square Ru/TiO₂ ;
 \blacktriangle K-Ru/SiO₂ ; \bullet K-Ru/Al₂O₃ ; \blacksquare K-Ru/TiO₂ .

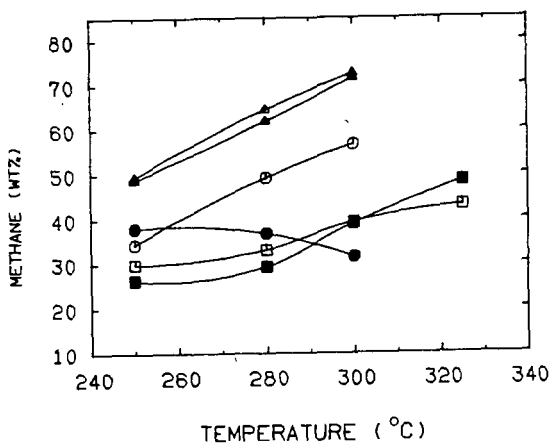


Figure 2 Temperature Dependence of CH₄ Formation.

TABLE 2

PROBABILITY OF CHAIN GROWTH ACCORDING TO
ANDERSON-SCHULZ-FLORY PLOT ^a

Catalyst	Probability	
	P _i	P _s
Ru/SiO ₂	0.39	0.38
K- Ru/SiO ₂	0.45	0.44
Ru/Al ₂ O ₃	0.41	0.42
K- Ru/Al ₂ O ₃	0.53	0.53
Ru/TiO ₂	0.50	0.50
K- Ru/TiO ₂	0.50	0.50

a. Reaction at 280°C, H₂/CO = 1, and GHSV = 1800 hr⁻¹

Both ion-exchanged and impregnated RuNaY catalysts produced predominantly methane. The addition of K increased the olefin fraction by an order of magnitude for the impregnated RuNaY but it had no effect for that of the ion-exchanged catalyst. Since the ion-exchanged RuNaY is highly dispersed (> 60%) and with Ru predominantly inside the zeolite crystal, the Ru, therefore, is probably not accessible to the impregnated potassium salt. This can also be verified by comparing the activation energy of the reaction for both the unprompted and the promoted catalysts. It was found that the activation energy for CO conversion decreased between 20 to 50% after K addition for all the Ru catalysts except ion-exchanged RuNaY. For ion-exchanged RuNaY, it remained unchanged (ca. 22 Kcal/gmole). It has been postulated that the addition of K decreases the activation energy of the F-T reaction on Fe by causing a lowering of the local ionization energy in the vicinity of an adsorbed K atom. (12)

The most significant change in hydrocarbon selectivity was found on graphite-supported Ru catalysts. The unprompted Ru/graphite produces essentially only paraffins in the C₂-C₄ range while the K-Ru/graphite produced mainly olefins, surprisingly 82% of the total C₂-C₄ hydrocarbons produced was propylene. Previous research of K promotion on the Ru₃(CO)₁₂/Al₂O₃ catalyst has indicated that the maximum propylene produced from the F-T synthesis was 42% in total C₂-C₄ hydrocarbons. (5) The fact that the graphite is an electron conductor may be involved in this effect. Ozaki (6) and Sagert and Poutesu (7) have suggested that the electron density of the transition metal may have increased when it is supported on graphite. Addition of K to the Ru/graphite probably enhanced this effect.

CONCLUSION

The addition of a potassium promoter can greatly affect the catalytic properties of Ru in the F-T reaction, depending on the support chosen. It enhances olefin formation and higher hydrocarbon production for the traditional Al₂O₃- and SiO₂-supported Ru. On Ru/graphite at 1 atm, it preferentially promotes propylene formation. Potassium enhances by about 20% the olefin production over Ru/TiO₂ in the temperature range 250°C to 325°C. As a result of alkali promotion of the Ru catalysts, the olefin fraction of the C₂-C₄ hydrocarbons produced becomes a weak function of the reaction temperature. Further study is needed to delineate the promoter-metal-support interactions.

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